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(12) **United States Patent**
Schut et al.(10) **Patent No.:** **US 9,447,299 B2**(45) **Date of Patent:** **Sep. 20, 2016**(54) **INKS FOR 3D PRINTING GRADIENT
REFRACTIVE INDEX (GRIN) OPTICAL
COMPONENTS****G02B 1/04** (2006.01)**G02B 3/00** (2006.01)**G02B 27/00** (2006.01)**B33Y 70/00** (2015.01)(71) Applicant: **VOXTEL, INC.**, Beaverton, OR (US)(72) Inventors: **David M. Schut**, Philomath, OR (US);
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(US)(73) Assignee: **Voxel, Inc.**, Beaverton, OR (US)(*) Notice: Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.(21) Appl. No.: **14/888,533**(22) PCT Filed: **May 2, 2014**(86) PCT No.: **PCT/US2014/036660**

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61/818,534, filed on May 2, 2013, provisional
application No. 61/819,104, filed on May 3, 2013.(51) **Int. Cl.****C09D 11/38** (2014.01)**C09D 11/101** (2014.01)**C08K 3/22** (2006.01)**C08K 3/28** (2006.01)**C08K 3/34** (2006.01)**C08K 7/26** (2006.01)**C08K 9/02** (2006.01)(52) **U.S. Cl.**CPC **C09D 11/38** (2013.01); **C08K 3/22**(2013.01); **C08K 3/28** (2013.01); **C08K 3/34**(2013.01); **C08K 7/26** (2013.01); **C08K 9/02**(2013.01); **C09D 11/101** (2013.01); **G02B****1/041** (2013.01); **G02B 3/0087** (2013.01);**G02B 27/0062** (2013.01); **B33Y 70/00**(2014.12); **C08K 2003/2241** (2013.01); **C08K****2003/2244** (2013.01); **C08K 2003/282**

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See application file for complete search history.

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(57)

ABSTRACTOptical inks suitable for 3D printing fabrication of gradient
refractive index (GRIN) optical components are composed
of a monomer matrix material [100] in which ligand-
functionalized nanoparticles [102] are well dispersed at
more than 2% loading to induce a change in the index of
refraction of the matrix of at least 0.02. The ligands are less
than 1.2 nm in length and are covalently bonded to both the
nanoparticles and the monomer matrix. The nanoparticles
are less than 100 nm in size and the doped matrix material
has a transmittance of at least 90% at wavelengths of
interest. The matrix material has less than 20 cPoise viscos-
ity and is UV crosslinkable to form a cured polymer.**5 Claims, 2 Drawing Sheets**

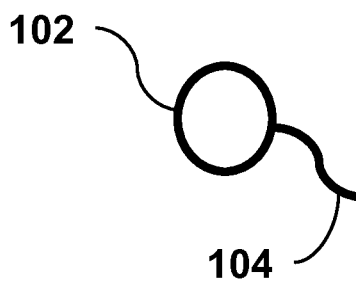
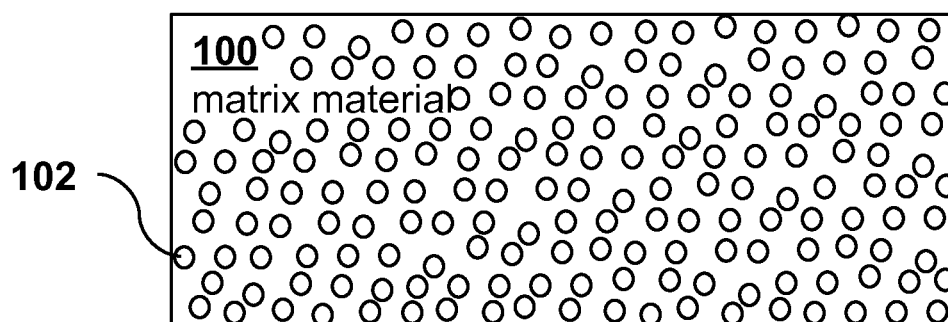
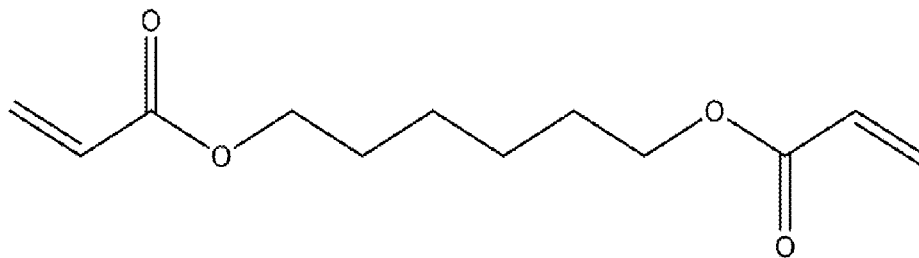
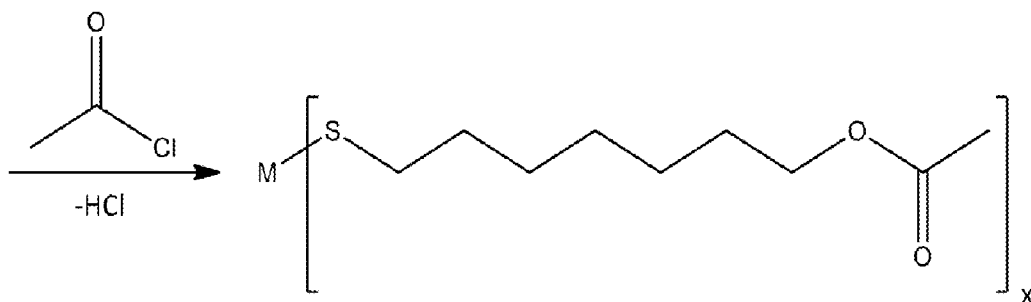
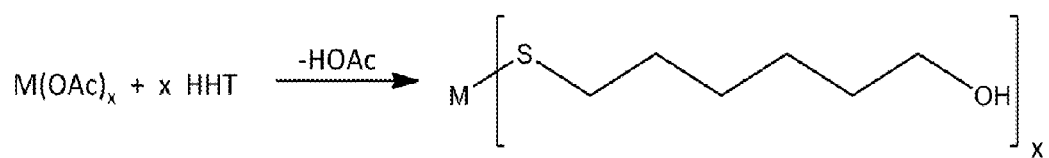
Fig. 1A**Fig. 1B**

Fig. 2**Fig. 3**

INKS FOR 3D PRINTING GRADIENT REFRACTIVE INDEX (GRIN) OPTICAL COMPONENTS

FIELD OF THE INVENTION

The present invention relates generally to optical ink compounds. More specifically, it relates to inkjet-printable optical ink compositions suitable for 3D printing of gradient refractive index (GRIN) optical components.

BACKGROUND OF THE INVENTION

Gradient refractive index (GRIN) optical structures are composed of an optical material whose index of refraction, n , varies along a spatial gradient in the axial and/or radial directions of the lens. They have many useful applications such as making compact lenses with flat surfaces.

There are several known techniques for fabricating GRIN lenses. One approach is to press films of widely varying refractive indices together into a lens using a mold, e.g., as taught in U.S. Pat. No. 5,689,374. This process, however, is expensive to develop. A second approach for fabricating GRIN lenses is to infuse glass with ions at varying density. This approach has reached commercial production, but it is also expensive and effectively limited to small radially symmetric lenses by the depth to which ions will diffuse into glass. A third approach for fabricating GRIN lenses is to use 3D printing technology with inks composed of a polymer matrix doped with particles which change the index of refraction of the matrix. Each printed droplet has a distinct refractive index controlled by the concentration of dopants in the polymer material. This approach is described, for example, in R. Chartoff, B. McMorrow, P. Lucas, "Functionally Graded Polymer Matrix Nano-Composites by Solid Freeform Fabrication", Solid Freeform Fabrication Symposium Proc., University of Texas at Austin, Austin, Tex., August, 2003, and in B. McMorrow, R. Chartoff, P. Lucas and W. Richardson, 'Polymer Matrix Nanocomposites by Inkjet Printing', Proc. of the Solid Freeform Fabrication Symposium, Austin, Tex., August, 2005.

Although using 3D printing has the potential to provide an efficient and inexpensive means of fabricating GRIN lenses, a number of unsolved problems have prevented or significantly limited its practical realization. One of the most significant problems is that the ink compounds need to simultaneously have all the desired properties for high quality GRIN lenses while at the same time need to have properties suitable for 3D printing using inkjet technology. In particular, it is important that the doping of the host matrix creates a substantial change in the index of refraction of the host matrix, so that the GRIN lens can efficiently provide significant optical power. It is also important that the material, both when doped and undoped, be substantially transparent at wavelengths of interest (e.g., visible spectrum) so that light is transmitted through the lens rather than absorbed. At the same time, in order to be suitable for the 3D printing process, the ink material must have a low viscosity both with and without doping, and be curable by a process that does not create uncontrollable distortion of the printed lens. Despite the desirability for an ink satisfying all of these criteria, researchers have yet to understand what physical characteristics of matrix and dopant materials are sufficient to produce inks satisfying all these properties, or to discover any specific ink compounds that simultaneously possess all

these properties. As a result, the realization of 3D printing of high quality GRIN lenses remains elusive.

SUMMARY OF THE INVENTION

The present inventors have clearly specified for the first time the key physical characteristics of matrix materials and dopants that are sufficient to provide all the important properties suitable for 3D printing of high quality GRIN lenses. They have also discovered and described herein a variety of specific examples of such ink compounds. These inks have the following key physical characteristics. The matrix material is a monomer that is UV crosslinkable with 20% or less shrink to minimize the strain and subsequent deformation of the optical structure. The matrix material has a transmittance of at least 90% (preferably at least 99%) at the wavelengths of interest, and the viscosity of the matrix in its monomer form is less than 20 cPoise so that it can be inkjet printed. The matrix material is doped with nanocrystal nanoparticles at a loading of at least 2% by volume. The nanocrystals are selected such that a difference in index of refraction between the doped and undoped matrix material is at least 0.02, i.e., $\Delta n \geq 0.02$. The nanocrystal sizes are sufficiently small that they do not induce Mie or Rayleigh scattering at the wavelengths of interest (e.g., less than 50 nm in size for visible wavelengths, less than 100 nm for IR wavelengths). The nanocrystal material, as well as the doped matrix material, preferably has a transmittance of at least 90% (more preferably, at least 99%) in a predetermined optical wavelength range (e.g., visible spectrum). The nanocrystals are functionalized with ligands selected to ensure that the nanocrystals are well dispersed in the matrix. Specifically, each ligand is less than 1.2 nm in length, is covalently bonded at its anchor end to the nanocrystal, and is covalently bonded at its buoy end to the monomer so that good dispersion is maintained during polymerization. In addition, the buoy ends of the ligands repel each other to help prevent aggregation and light scattering, resulting in less than 5% scattering from aggregated nanoparticle clusters. These physical characteristics provide guidance to those skilled in the art to identify a class of inks suitable for 3D printing of GRIN lenses. A number of examples of such inks are described herein.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1A: Cross-sectional schematic diagram of an optical ink composed of a matrix material doped with nanoparticles, according to an embodiment of the invention.

FIG. 1B: Schematic diagram of a nanoparticle functionalized with a ligand, according to an embodiment of the invention.

FIG. 2: Chemical structure of HDODA (1,6-hexanediol diacrylate).

FIG. 3: Scheme for an alternate synthetic route to metallic salts of HHT.

DETAILED DESCRIPTION

Embodiments of the present invention include optical inks suitable for use in fabricating GRIN lenses using 3D printing technology such as standard drop-on-demand inkjet printing. These inks may also be used to fabricate GRIN lenses using other printing techniques such as screen printing, tampo printing, aerosol jet printing, and laser cure printing. The optical inks prepared according to embodiments of the present invention are composed of a matrix

material composed of a monomer and nanoparticles dispersed in the matrix material. The nanoparticle-doped monomer matrix material (a liquid) is placed in an inkjet printhead. In addition, an adjacent inkjet printhead is filled with undoped matrix material. Additional printheads may also be filled with another optical ink with a different type or concentration of nanoparticle. Drop-on-demand inkjet printing technology is used to create microscopic, on-the-sample mixtures of the two (or more) liquids, thereby creating precisely-controlled and highly-localized regions having optical index controlled by the mixture of the undoped and doped inks. The localized composition and three dimensional structure is locked-in by polymerizing the monomeric solution into an optical-quality polymer. Each droplet of polymer that is deposited onto the substrate on which the GRIN lens is being formed, can be created with a desired concentration of nanoparticles. The volumetric concentration of nanoparticle within a given droplet volume determines the effective refractive index of that material. Drop on demand printing, such as inkjet printing, allows for the formation of three dimensional structures where different volumes within the structure contain different concentrations of dopants to effectively change the refractive index within a three dimensional structure. The creation of precise three dimensional optical lenses and other optical structures by stereolithography is known to those skilled in the art of GRIN lens design. Embodiments of the present invention provide inks suitable for the practical realization of such 3D printable inks for high quality GRIN lens fabrication. These inks provide the ability to control the index of refraction in three dimensions for creating large, localized index changes while maintaining high optical transmission and freedom from deleterious scattering phenomena.

Since drop-on-demand inkjet may utilize multiple printheads with different loading of the index-changing dopant, the inks provided by the present invention may be used in various combinations with each other as well as with other optical inks. The ability to alter, in three dimensions, the index of refraction both above and below that of the host matrix opens the design space for GRIN optical components.

According to embodiments of the present invention, an optical ink is composed of a matrix material **100** doped with nanoparticles **102**, as shown in FIG. 1A. The matrix **100** is composed of a monomer that is capable of being UV cured to create a solid polymer, and the nanoparticles **102** are each functionalized with a ligand **104**, as shown in FIG. 1B.

The matrix material **100** is a monomer that is UV cross-linkable. Preferably, the UV curing results in at most 20% shrink, which serves to minimize the strain and subsequent deformation of the optical structure. The viscosity of the matrix **100** in its monomer form is less than 20 cP so that it can be inkjet printed. When cured, the matrix material **100** preferably has a transmittance of at least 90% (preferably at least 99%) at the wavelengths of interest (e.g., visible spectrum).

Dispersed within the matrix **100** are nanoparticles **102** which preferably are nanocrystals. The nanoparticles **102** are present in the matrix **100** at a loading of at least 2% by volume, altering the index of refraction of the undoped matrix by at least 0.02, i.e., $\Delta n \geq 0.02$. In addition, in order to preserve transparency of the ink, the nanoparticles **102** are made sufficiently small that they do not induce Mie or Rayleigh scattering at the wavelengths of interest. For example, for GRIN lenses designed to operate in the visible spectrum, the sizes of the nanoparticles **102** are less than 50 nm. For operation in the infrared spectrum, the sizes are less

than 100 nm. In addition, also to help preserve transparency, the nanoparticles **102** are preferably made of materials that transmit greater than 90% (preferably greater than 99%) of the light in a predetermined optical wavelength range (e.g., visible or infrared). In order to achieve more than 2% loading and large Δn while also providing a well-dispersed doping (and transparency), the nanoparticles **102** are functionalized with ligands **104** that are less than 1.2 nm in length. In addition, each ligand **104** is covalently bonded at its anchor end to the nanocrystal **102**, and is covalently bonded at its buoy end to the monomer material of the matrix **100**. In addition, the buoy ends of the ligands **104** preferably repel each other to help prevent aggregation and light scattering, resulting in less than 5% scattering from aggregated nanoparticle clusters. These physical characteristics of the ligands ensure that the nanoparticles **102** are well dispersed in the matrix and that good dispersion is maintained during polymerization.

These inks will now be further described and illustrated in the context of several concrete examples. Those skilled in the art will appreciate that the principles, teachings, and techniques discussed in the following examples are not limiting but in fact provide further illustration of the range of possible inks that are encompassed within the scope of the invention.

According to one embodiment of the invention, the matrix or host polymer is 1,6-hexanediol diacrylate (HDODA), and the nanoparticle is an organometallic compound. The organometallic compound may be, for example, any of various salts of metals such as zinc (Zn^{2+}), lead (Pb^{2+}), titanium (Ti^{4+}), and other metallic salts that are clear and transparent. More generally, the metallic salt may have a cation consisting of Ti^{4+} , Pb^{2+} , Zn^{2+} , Al^{3+} , Sn^{4+} , In^{3+} , Ca^{2+} , Ba^{2+} , Sr^{2+} , Y^{3+} , La^{3+} , Ce^{3+} , Nd^{3+} , Pr^{3+} , Eu^{3+} , Er^{3+} , Yb^{3+} , Gd^{3+} , Ho^{3+} , Sm^{3+} , Tb^{3+} , Dy^{3+} , Tm^{3+} , Zr^{4+} , Hf^{4+} or Ta^{5+} .

Ligand functionalization of clear, transparent metallic salts provide matrix compatibility with HDODA, allowing high density loading of the organometallic salt into the matrix. Furthermore, due to a difference of index of refraction between undoped HDODA and HDODA doped with the functionalized metallic salt, GRIN lenses may be formed using drop-on-demand printing techniques such as inkjet printing. The metallic salts interact favorably with a host matrix material such that greater than 90% transparency is obtained in the spectral region spanning 375 nm through 1600 nm.

As shown in FIG. 2, HDODA is a well-known material for the fabrication of clear coatings. It has a low viscosity (7.9 cP) making it amenable towards dispensing using drop-on-demand techniques such as inkjet printing. It also has a large spectral window in which greater than 99% transparency is observed, making it ideal to construct lensing material. HDODA also has an index of refraction of 1.456. By using an organometallic compound having an index of refraction different from that of HDODA, using drop-on-demand techniques such as inkjet printing, gradient refractive index lenses may be fabricated having control of the index of refraction in three dimensions.

In order for the nanoparticle to be successfully incorporated into an HDODA solution, it must have a ligand chemistry (surface treatment) that is compatible with the HDODA. To do this, a ligand mimicking the host matrix material can be utilized to ensure that metallic salts can be incorporated into the HDODA without undergoing phase segregation, precipitation, or other means of separation from the host material.

As examples, an ink formulation may use a metal-ligand placed in 1,6-hexanediol diacrylate at 1-75 wt % with 0.1-5.0 wt % Irgacure 184 and 0.1-5.0 wt % Irgacure 819. Another ink formulation may use a metal-ligand placed in 1,6-hexanediol diacrylate at 1-75 wt % with 0.1-5.0 wt % Irgacure 184 and 0.1-5.0 wt % Irgacure 819. Another ink formulation may use a metal-ligand placed in 1,6-hexanediol diacrylate at 1-75 wt % with 0.1-5.0 wt % Irgacure 184 and 0.1-5.0 wt % Irgacure 819. Yet another ink formulation that may use a metal-ligand mixture placed in 1,6-hexanediol diacrylate at 1-75 wt % with 0.1-5.0 wt % Irgacure 184 and 0.1-5.0 wt % Irgacure 819.

A route to obtaining the material to print this lens uses the alcohol terminated ligands as shown in reaction sequence depicted in FIG. 3.

According to another embodiment, stereolithographic techniques are used to print in 3D using droplets of the monomeric form of optical polymers (such as 1,6-Hexanediol diacrylate, aka HDDA or HDODA, or styrene) doped with varying levels of nanoparticles having an index refraction that is significantly different from that of the optical polymer. With each droplet being able to deliver a distinct refractive index, this technology allows true 3D creation of GRIN optical elements of arbitrary shape. A challenge in the past has been the limited selection of nanosized materials which are both transparent in the optical range of interest and have a significant difference in refractive index, as compared to optical polymers whose refractive index typically falls between that of polystyrene and of poly methyl methacrylate (1.592 and 1.489 respectively). According to this embodiment, diamond is used as the nanoparticle material. It has an optical window spanning from about 0.25 microns to 80 microns and a refractive index of 2.42, which is large compared to most optical polymers. Recently-developed diamond nanocrystals have dimensions less than one tenth the wavelength of light (i.e., less than or equal to 50 nm diameter particles for visible light), which minimizes Mie or Rayleigh scattering. Using drop-on-demand techniques such as inkjet printing, gradient refractive index optical components may be fabricated having control of the index of refraction in three dimensions.

The diamond nanoparticles are first coated with a ligand material which provides chemical compatibility with the optical polymer, then blended with the monomeric form of the optical material, delivered using 3D printing technology, and finally polymerized into transparent solids which serve as GRIN optical structures. Arbitrarily 2D and 3D GRIN optical components are fabricated by drop-on-demand stereolithographic inkjet printing or by other printing techniques.

Nanodiamonds are commercially available as byproducts of refineries, mining operations and quarries and are broken down to smaller sizes through ball milling and sonication. Alternately detonation nanodiamond (DND), often also called ultradispersed diamond (UDD), is diamond that originates from a detonation of an oxygen-deficient explosive mixture of TNT/RDX. In both cases particles of 4-6 nm are obtained.

For the diamond nanomaterial to be successfully incorporated into an optical polymer matrix, it is provided with a surface treatment (i.e., ligand) that is compatible with the polymer. The ligand is described by analogy with anchor-chain-buoy configuration in which the "anchor" end of the ligand molecule is the chemical entity that covalently binds to the surface of the diamond nanoparticle, the "buoy" at the other end is the entity which provides chemical compatibility with polymeric matrix, and the "chain" refers to the

length of the linkage between the two previously mentioned entities. Carboxylates, amines, thiol groups may provide the anchor entity for bonding to the carbon-based nanodiamonds. The buoy group is selected to match the chemical nature host optical polymer, for example an acetylacrylate group for compatibility with acrylate-based polymers, and disperse the functionalized nanoparticles by repelling other buoys. Minimal chain lengths of 2-4 carbon atoms are effective for dispersing nanoparticles in the size range from 2-20 nm.

In a preferred embodiment, the appropriately-coated diamond nanoparticles are blended with the monomeric form of the optical polymer with a specified percent loading. The nanoparticle-doped liquid is placed in an inkjet printhead, in tandem with an inkjet printhead containing pure monomer. This can be extended to multiple printheads with different percent particle loading. Drop-on-demand inkjet printing technology is used to create microscopic, on-the-sample mixtures of the two (or more) liquids, thereby creating precisely-controlled and highly-localized regions of variable optical index. The localized composition and three dimensional structure is locked-in by polymerizing the monomeric solution into an optical-quality polymer. This optical ink thus provides the ability to concurrently modify the index of refraction in three dimensions by use of the doped nanoparticles, providing the means for creating large, localized index changes while maintaining high optical transmission and freedom from deleterious scattering phenomena.

According to another embodiment of the invention, stereolithographic techniques are used to print in three dimensions using droplets of the monomeric form of optical polymers (such as 1,6-Hexanediol diacrylate, aka HDDA, or styrene) doped with varying levels of nanoparticles having an index refraction that is significantly different from that of the optical polymer. With each droplet being able to deliver a distinct refractive index, this technology allows true 3D creation of GRIN optical elements of arbitrary shape. A challenge in the past has been the limited selection of nanosized materials which are both transparent in the optical range of interest and have a significant difference in refractive index, as compared to optical polymers whose refractive index typically falls between that of polystyrene and of poly methyl methacrylate (1.592 and 1.489 respectively). Although there are several transparent materials (such as TiO₂ and ZnS) with refractive index significantly higher than that of the polymer, there are very few materials with refractive index significantly lower than 1.5. According to this embodiment, microscopic hollow nanoparticles are used to effectively insert transparent, low refractive index "air-bubble" dopants into optical polymers for the fabrication of gradient refractive index (GRIN) optical components.

The index-changing hollow-sphere dopants are mixed with the monomeric form of the optical polymer to create stock solutions. Drop-on-demand inkjet printing of the stock solution, followed by rapid polymerization, yields gradient refractive index optical components with control of the index of refraction in three dimensions.

With air (or other gases) in their centers, the hollow microspheres have a broad optical transmission window and an (interior) refractive index of 1.0, which is significantly smaller than that of most optical polymers. If the shell of the microsphere has a refractive index matched to that of the optical polymer matrix, it is the just the interior dimension which needs to be less than or equal to one tenth the wavelength of light to avoid Mie or Rayleigh scattering. The hollow nanoparticles may be created via a micro-emulsion technique, then coated with a ligand material which provides

chemical compatibility with the optical polymer, blended with the monomeric form of the optical material, and finally polymerized into transparent solids. Arbitrarily 2D and 3D GRIN optical components are fabricated by drop-on-demand sterolithographic inkjet printing or by other printing techniques.

The nanoparticles in some embodiments may be hollow nanospheres or any carbon nanostructure (tube, buckyball, nanodiamond, etc.) with a gaseous or empty core. Polymeric and inorganic-shelled hollow microspheres may be fabricated using micro-emulsion techniques, yielding microspheres of sizes down to 100 nm. To minimize Mie or Rayleigh scattering dimensions are preferably less than one tenth the wavelength of light (e.g., at most 50 nm diameter particles for visible light). If the refractive index of the shell material is matched to that of the polymeric host, it is only the interior dimension that encompasses the low index gas that needs to be at or below one tenth the wavelength of light.

In order for the nanomaterial to be successfully incorporated into an optical polymer matrix, it is provided with a surface treatment (using ligand chemistry) that is compatible with the polymer. Carboxylates, amines, thiol groups provide the anchor entity for bonding to the carbon-based nanodiamonds. The buoy group is selected to match the chemical nature host optical polymer, for example an acrylate group for compatibility with acrylate-based poly-

mers. Minimal chain lengths of 2-4 carbon atoms are effective for dispersing nanoparticles in the size range from 2-20 nm.

The invention claimed is:

1. An optical ink composed of a monomer matrix material doped with ligand-functionalized nanoparticles; wherein the monomer has a viscosity less than 20 cPoise and is UV curable to form a solid polymer; wherein the matrix material doped with the ligand-functionalized nanoparticles has a transmittance of at least 90% in a predetermined optical wavelength range, wherein the ligand-functionalized nanoparticles have a size less than 100 nm, are loaded in the monomer matrix material at a volume percent of at least 2%, and alter an index of refraction of the monomer matrix by at least 0.02; wherein each of the ligand-functionalized nanoparticles is covalently bonded to a ligand, where the ligand is covalently bonded to the monomer matrix material, and has a length less than 1.2 nm.
2. The optical ink of claim 1 wherein buoy ends of the ligands repel each other.
3. The optical ink of claim 1 wherein the ligand-functionalized nanoparticles have a size less than 50 nm.
4. The optical ink of claim 1 wherein the nanoparticles are ligand modified metallic salts, nanocrystal diamond, nanocrystal microspheres, or a hollow nanomaterial.
5. The optical ink of claim 1 wherein the monomer matrix is composed of 1,6-hexanediol diacrylate, or an acrylate optical polymer.

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